Crystal structure of bis(μ_2-thiocyanato)tetrakis(3,5-dimethyl-1-(thiocarbamoyl)pyrazole)dinickel(II) dichloride ethanol disolvate, $[Ni(NCS)_2(C_6H_6N_3S)_4][Cl]_2 \cdot 2C_2H_5OH$

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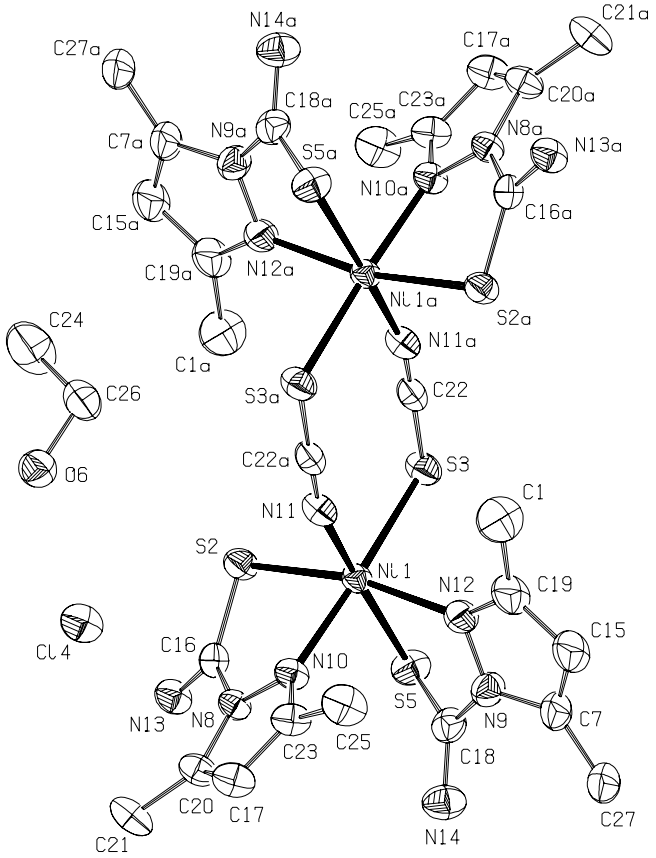

Abstract

$C_{30}H_{48}Cl_2N_{14}Ni_2O_2S_6$, monoclinic, $P12_1/c1$ (no. 14), a = 12.0407(7) Å, b = 11.8861(6) Å, c = 15.7389(9) Å, β = 93.904(1)°, V = 2247.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.032, $wR_{ref}(F^2)$ = 0.069, T = 120 K.

Source of material

The complex was synthesized by mixing hot ethanolic solution of the ligand 3,5-dimethyl-1-thiocarboxamide pyrazole (Pz-CS, 1 mmol) and $NiCl_2 \cdot 6H_2O$ (0.5 mmol). The solution was filtered and the filtrate left to crystallize. The precipitated crystals were separated by filtration.

Elemental analysis – found: C, 34.40 %; H, 4.64 %; N, 19.09 %; calc. for $C_{30}H_{48}Cl_2N_{14}Ni_2O_2S_6$: C, 35.41 %; H, 4.75 %; N, 19.27 %.

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Discussion

As a part of systematic study on complexing properties of pyrazolyl molecules [1-3], the present paper reports on a new Ni(II) complex.

The crystal structure of the ligand 3,5-dimethyl-1-thiocarboxamide pyrazole ($L1$) was recently reported [4] and a DFT computation has been used to obtain in-vacuo theoretical geometry [5]. The interesting aspect of this ligand and its derivative is its ambidentate nature. It can coordinate bidentately to metal through the pyrazole ring nitrogen and thiolato sulfur or by using ring nitrogen and iminyl nitrogen (of thiocarbamyl group). Explanation of the ambidentate nature of this ligand in terms of the HSAB model [6] implies its capability to stabilize different oxidation state of the same metal. It could be also expected that oxidation state of the ligand would influence the mode of coordination. It was found that in the case of Co(III)(L)$_3$ complex [7], monodeprotonated $L1$ is bound to metal through the pyrazole ring nitrogen and the thiocarboxamide nitrogen. However, in the $Co_2L_2Cl_4$ five-coordinated Co (II) is bound to neutral $L1$, through the pyrazole nitrogen and thiol sulfur. In accordance with the HSAB model [8], it is expected that ligand $L1$ will bind to Ni(II) through the pyrazole nitrogen and sulfur from the thiocarboxamide fragment. This mode of coordination was observed in the Ni(II) complex with the closely related monodeprotonated ligand 3,5-dimethyl-1-(*N*-ethyl)-thiocarbamylpyrazole ($L2$) [9]. In contrast to this, recent X-ray powder diffraction study [10] revealed that monodeprotonated ligand $L1$ is bound to Ni(II) through the nitrogen atoms of the pyrazole ring and the thiocarboxamide group. This observation is not in accordance with the expectations based on HSAB model, which stress the importance of obtaining more information on the factors important for complexing properties of this ligand.

The crystal structure of the title compound is built up of discrete centrosymmetric dinuclear units, with end-to-end bridging NCS^- anionic ligands, Cl^- anions, and ethanol molecules. Two neutral molecules of $L1$ coordinate to Ni(II) through the pyrazole-ring N atoms and thiocarboxamide S atoms, which is in accordance with the HSAB model. The Ni(II) adopts distorted octahedral coordination, with thiocyanato N, and thiol S placed in the axial positions. Two pyrazolyl ligands show similar arrangement, except for the torsion angle N–N–C–S (∠N10–N8–C16–S2 = 14.66°, ∠N12–N9–C18–S5 = 32.44°), which indicates significant difference in the conformation of two chelate rings. Greater distortion of the chelate ring is associated with the longer axial Ni—S bond (d(Ni1—S5) = 2.519 Å, d(Ni1—S2) = 2.422 Å). Structural pa-

rameters of the two chelate rings differ significantly from those observed in square-planar Ni($L2$)$_2$ complex [10] and indicate weaker bonding. The bridging thiocyanate group is nearly linear and shows bent coordination modes with the metal atoms (∠S3–C22–N11 = 178.58°, ∠Ni1–S3–C22 = 102.40°, ∠Ni1–N11–C22 = 164.47°). Distance between the two nickel atoms is 5.578 Å. The packing of complex molecules is determined by the presence of free chloride anion, which ethanol molecule. Repulsion of the chloride anion lead to the arrangement of hydrogen bonded atoms in a tetrahedral fashion. The other important factor is the position of hydrogen bond donors in the complex molecule. Both hydrogen atoms at nitrogen N14 are involved in the hydrogen bonds with Cl, and formation of molecular chain, while the connection between the neighboring chains is achieved by the hydrogen bond involving atom N13 and chlorine. The angle between the two neighboring molecular chains is 69° (measured by the torsion angle formed by the lines connecting the centroids of the metallocycle rings). The crystal structure is additionally stabilized by the hydrogen bond involving ethanol molecule and nitrogen N13.

Table 1. Data collection and handling.

Crystal:	green prism, size 0.04 × 0.16 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.82 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART CCD, ω/φ
$2\theta_{max}$:	59.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	27632, 6381
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4062
$N(param)_{refined}$:	349
Programs:	SHELXS-97 [12], SHELXL-97 [13], ORTEP-3 [14], WinGX [15], ORTEP-II [16]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(5)	4e	0.661(2)	0.486(1)	–0.014(1)	0.040(2)
H(6)	4e	0.630(2)	0.463(1)	0.075(1)	0.041(2)
H(7)	4e	0.562(2)	0.062(1)	0.234(1)	0.033(2)
H(8)	4e	0.318(2)	0.128(3)	–0.001(1)	0.051(2)
H(9)	4e	0.452(2)	0.1934(9)	–0.118(1)	0.037(2)
H(10)	4e	0.751(2)	0.170(2)	–0.155(2)	0.056(2)
H(11)	4e	0.379(2)	0.062(2)	0.075(2)	0.051(2)
H(12)	4e	0.769(2)	0.598(2)	–0.099(2)	0.068(2)
H(14)	4e	0.487(1)	0.136(1)	0.180(1)	0.034(2)
H(15)	4e	0.362(2)	0.190(2)	0.081(2)	0.051(2)
H(16)	4e	0.986(1)	0.447(2)	–0.1622(9)	0.051(2)
H(17)	4e	0.895(2)	0.630(2)	–0.092(2)	0.068(2)
H(18)	4e	0.638(2)	0.185(2)	–0.207(1)	0.057(2)
H(22)	4e	1.060(3)	0.166(2)	–0.084(1)	0.084(2)
H(23)	4e	0.834(3)	0.610(2)	–0.010(1)	0.069(2)
H(25)	4e	0.976(2)	0.158(2)	–0.163(2)	0.084(2)
H(30)	4e	1.076(2)	0.239(2)	–0.164(2)	0.084(2)
H(34)	4e	0.695(2)	0.288(2)	–0.161(2)	0.057(2)
H(1)	4e	0.319(3)	0.384(2)	–0.163(2)	0.099(2)
H(2)	4e	0.196(2)	0.397(2)	–0.200(2)	0.098(2)
H(3)	4e	0.232(2)	0.261(2)	–0.303(1)	0.052(2)
H(4)	4e	0.401(3)	0.187(2)	–0.295(2)	0.051(2)
H(13)	4e	0.257(2)	0.210(2)	–0.211(1)	0.052(2)
H(241)	4e	0.296(3)	0.436(2)	–0.253(2)	0.099(2)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	4e	0.83558(3)	0.15012(3)	0.04438(2)	0.0158(1)	0.0200(2)	0.0178(1)	0.0011(1)	0.0042(1)	0.0010(1)
S(2)	4e	0.74876(5)	0.03482(6)	0.14810(4)	0.0182(3)	0.0267(3)	0.0200(3)	0.0018(2)	0.0019(2)	0.0055(2)
S(3)	4e	1.01656(5)	0.13779(6)	0.12758(4)	0.0179(3)	0.0264(3)	0.0260(3)	0.0009(2)	0.0015(2)	–0.0067(3)
S(5)	4e	0.79333(6)	0.31496(6)	0.13741(4)	0.0297(3)	0.0252(3)	0.0211(3)	0.0041(3)	0.0054(2)	0.0002(2)
N(8)	4e	0.5896(2)	0.1382(2)	0.0490(1)	0.0161(9)	0.023(1)	0.0151(9)	0.0011(8)	0.0037(7)	–0.0001(8)
N(9)	4e	0.8347(2)	0.3830(2)	–0.0187(1)	0.026(1)	0.021(1)	0.024(1)	0.0006(9)	0.0052(9)	0.0034(8)
N(10)	4e	0.6724(2)	0.1582(2)	–0.0058(1)	0.0180(9)	0.025(1)	0.0144(9)	0.0021(8)	0.0052(7)	0.0017(8)
N(11)	4e	0.8717(2)	0.0255(2)	–0.0362(1)	0.0164(9)	0.028(1)	0.023(1)	0.0004(9)	0.0021(8)	–0.0012(9)
N(12)	4e	0.8873(2)	0.2819(2)	–0.0309(1)	0.021(1)	0.024(1)	0.026(1)	0.0020(8)	0.0075(8)	0.0022(9)
N(13)	4e	0.5472(2)	0.0962(2)	0.1867(1)	0.021(1)	0.031(1)	0.019(1)	0.0017(9)	0.0053(8)	0.0035(9)
N(14)	4e	0.6762(2)	0.4548(2)	0.0350(2)	0.030(1)	0.031(1)	0.026(1)	0.008(1)	0.0052(9)	0.001(1)
C(1)	4e	1.0223(3)	0.2089(3)	–0.1286(2)	0.044(2)	0.045(2)	0.053(2)	0.007(2)	0.036(2)	0.013(2)
C(7)	4e	0.8717(2)	0.4652(2)	–0.0717(2)	0.025(1)	0.027(1)	0.035(2)	–0.005(1)	0.002(1)	0.011(1)
C(15)	4e	0.9471(2)	0.4136(3)	–0.1196(2)	0.027(1)	0.040(2)	0.040(2)	–0.002(1)	0.010(1)	0.018(1)
C(16)	4e	0.6210(2)	0.0923(2)	0.1295(2)	0.021(1)	0.019(1)	0.016(1)	–0.0029(9)	0.0018(8)	–0.0003(9)
C(17)	4e	0.5041(2)	0.1791(2)	–0.0748(2)	0.025(1)	0.035(2)	0.018(1)	0.005(1)	–0.0001(9)	0.000(1)
C(18)	4e	0.7635(2)	0.3903(2)	0.0489(2)	0.026(1)	0.020(1)	0.024(1)	–0.000(1)	0.003(1)	–0.004(1)
C(19)	4e	0.9535(2)	0.3001(3)	–0.0939(2)	0.025(1)	0.038(2)	0.030(1)	0.001(1)	0.012(1)	0.009(1)
C(20)	4e	0.4853(2)	0.1500(2)	0.0065(2)	0.018(1)	0.030(1)	0.019(1)	0.003(1)	–0.0014(8)	–0.004(1)
C(21)	4e	0.3763(2)	0.1303(3)	0.0432(2)	0.016(1)	0.046(2)	0.024(1)	0.000(1)	0.0005(9)	–0.005(1)
C(22)	4e	1.0834(2)	0.0425(2)	0.0744(2)	0.015(1)	0.026(1)	0.020(1)	–0.0031(9)	–0.0001(8)	0.003(1)
C(23)	4e	0.6205(2)	0.1832(2)	–0.0802(2)	0.024(1)	0.028(1)	0.016(1)	0.005(1)	0.0014(9)	0.0009(9)
C(25)	4e	0.6816(3)	0.2091(3)	–0.1578(2)	0.032(1)	0.044(2)	0.019(1)	0.004(1)	0.005(1)	0.006(1)
C(27)	4e	0.8388(3)	0.5859(3)	–0.0673(2)	0.027(1)	0.030(2)	0.059(2)	–0.006(1)	–0.002(1)	0.017(2)
O(6)	4e	0.3921(2)	0.2465(2)	–0.2682(1)	0.027(1)	0.029(1)	0.030(1)	0.0005(8)	0.0032(8)	0.0013(8)
C(24)	4e	0.2717(3)	0.3805(3)	–0.2140(3)	0.036(2)	0.052(2)	0.079(3)	–0.005(2)	0.013(2)	–0.035(2)
C(26)	4e	0.2792(2)	0.2670(3)	–0.2505(2)	0.023(1)	0.035(2)	0.050(2)	–0.003(1)	0.003(1)	–0.005(1)
Cl(4)	4e	0.54856(6)	–0.03139(6)	0.36392(4)	0.0274(3)	0.0378(4)	0.0213(3)	0.0030(3)	0.0042(2)	0.0022(3)

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